# Carbide precipitation by Heating High-Manganese Steel after Solution Treatment

# Carbide precipitation by Heating High-Manganese Steel after Solution Treatment*

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(Received February 22, 1962)

**Synopsis**

Carbide precipitations in isothermally and continuously heated Hadfield steel after solution-treatment were studied. Results obtained were as follows: 1. Solution-treated steel precipitated primary carbide isothermally in accordance with C-curve which has the nose at about 650～700°C, and also precipitated secondary pearlitic constituent isothermally with C-curve which has the nose at about 600°C. 2. At the primary stage, carbide films were formed at austenitic grain boundaries. In the low temperature range, carbide film formation delayed markedly, and then, platelet carbide were formed along the cleavage plane of grains. In the high temperature range, carbide films changed into granular particles and gradually took coherent shapes. 3. The nucleations of pearlitic constituents were most rapid at about 600°C, but growing velocity of pearlite has maximum value at about 500°C. 4. Secondary precipitates, pearlitic constituents, were very fine lamellar pearlite, and the lower temperature precipitates has the finer lamellar structure than precipitates at higher temperature. 5. In continuous heating, steel precipitated boundary carbides, platelet carbides and pearlitic constituents at about 500～600°C. It suggested that no pearlite precipitated when heated at a rate of above about 15°C/min and also no carbide precipitated when heated at a rate of above about 45°C/min. 6. Mechanical properties were injured by heating above about 350°C, since platelet carbide precipitations began at that temperature. Tensile strength lowered to minimum value at 750°C, since carbide films markedly grew at that temperature, and impact value, elongation and reduction of area lowered to minimum value at pearlite precipitation range. Increased hardness was affected mainly by platelet carbide precipitations.

## I. Introduction

It is well known that both the strength and the toughness of hadfield Mn steel are lowered pronouncedly by the carbide precipitation at grain boundaries caused by heating after solution treatment, though it has found extensive applications for its wear resistance and nonmagnetic character. Consequently, it is strictly prohibited[1] to heat it above 260°C in the process of manufacturing except the case where the solution treatment is possible after this stage, and it is not appropriate to use it in such a part as wear resistance area where temperature is raised to a high degree.

Meanwhile, Bühler et al.[2] evidenced the presence of the greatest residual tension in solution-treated Hadfield steel bar, and it is certain that an extremely great internal tension is present in heavy duty steel casting by the solution

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* The 1044th report of the Research Institute for Iron, Steel and Other Metals.

(1) H. S. Avery and M. J. Day, Metals Hand Book ASM (1948), 526.

(2) H. Bühler u. E. Herrman, Arch. Eisenhüt., **27** (1956), 269.

treatment. At present, it is impossible to perform any stress release treatment except heating for a long time at low temperature because of carbide precipitations. Concerning carbide precipitation by reheating austenitic high-Mn steel, Krivobok[3], Murakami and Mikami[4], and others[5]-[7] have reported. Irvine and Peckering[8], Kôri[9], Smith[10], Hashiura and Watanabe[11], Suzuki, Takada and Kusuoka[12] have recently reported on the same subject. In the present experiment, isothermal and continuous heating of standard Hadfield steel after solution-treatment were performed for the purpose of developing a new field of application of high-Mn steel.

## II. Experimental method

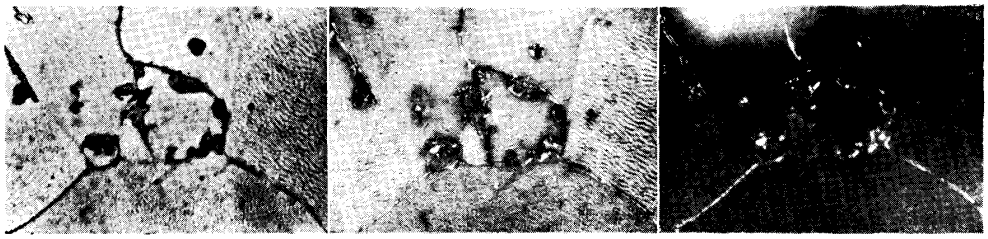
Specimens were prepared by melting 20 kg of steel ingot in a high frequency furnace, and by hot rolling into 20 mm diameter bars after forging into 50 mm square rods. According to chemical analyses they contained 1.20 per cent of C, 0.24 per cent of Si and 13.71 per cent of Mn. Round bars were again rolled into 12 mm square rods, 10 mm diameter bars and 8 mm diameter bars to be used for Charpy impact test, tensile test, microstructural test and dilatation test respectively. Specimens for tensile test were 7 mm$\phi$×35 mm at the parallel part, and those for impact test were smaller than the standard specimen in effective cross-sectional area with a U-notch 3 mm depth because of large absorption energy of high Mn steel. Specimens for microstructural test were 10 mm$\phi$×3 mm. Solution treatment was performed at 1050°C×1/2 hr in vacuum and *W.Q.*; lead bath was also used for short-time isothermal heating.

Carbide precipitation was determined mainly by microstructure and occasionally by hardness tester, differential dilatometer, high temperature microscope, electron microscope and simple magnetic analysis. Special attentions were paid to the treatment of specimens for microstructure regarding variations in the surface such as decarburization and the loss of manganese content, and microscopic polishing was performed after the surface layer of specimen had been ground off.

High Mn steels have so great work-hardening capacity that it tends to produce a thin layer of strain marking on the surface after the polishing in microstructural test[13], making it hard to detect the inter granular precipitate of carbide and producing a tough surface skin by etching. For these reasons, electropolishing was used throughout the experiments. For electropolishing solute, a mixture containing

(3) V. N. Krivobok, Trans. A.S.S.T., **15** (1929), 893.
(4) T. Murakami and M. Mikami, Tetsu-to-Hagane, **17** (1931), 205; Kinzoku-no-Kenkyu, **7**(1930), 219.
(5) T. Murakami and K. Hatsuta, Kinzoku-no-Kenkyu, **8** (1931), 132.
(6) E. C. Bain, E. S. Davenport and W. N. S. Waring, Trans. A. I. M. E., **100**(1932), 228.
(7) T. Murakami and T. Yashima, Kinzoku-no-Kenkyu, **10** (1933), 148.
(8) K. J. Irvine and F. B. Pickering, Iron and Steel, **29** (1956), 135.
(9) I. Kôri, Denkiseiko, **28** (1957), 6, 442.
(10) A. E. W. Smith, J. Iron & Steel Inst., **186** (1957), 425.
(11) K. Hashiura and M. Watanabe, J. Japan Inst. Met., **22** (1958), 557.
(12) A. Suzuki, H. Takada and S. Kusuoka, Kobe-Seiko, **9** (1959), No. 2, 57.
(13) Z. Nishiyama, Sci. Rep. Tôhoku Imp. Univ. I, **24** (1935), 128.

185 cc of perchloric acid with specific gravity 1.61, 765 cc of anhydride acetic acid and 50 cc of distilled water was used. With Al plate as cathode and at the primary voltage of 75 V and current density $4 \sim 5$ A/dm$^2$, electrolysis was performed for about 1 minute with an extremely good result. Electrolysis was performed immediately after polishing with emery paper No. 0, by which the polished surface could be obtained in the absence of precipitate, although the matrix of austenite was electropolished when precipitate was present at the grain boundaries or internal grains, but precipitate remained as it was. Thus the form of micro-precipitate could easily be observed by microscope. Microscopic examination of the electropolished surface in the dark field revealed even a small amount of precipitate for it was luminous as shown in Photo. 1.



Light field Medium dark field Dark field
× 1,500 (1/2)

Photo. 1. Observation of precipitates, 500°C × 2hr.

## III. Experimental result and consideration

1. Precipitation through isothermal heating

Though many reports have been made on the effect of reheating of high Mn steel, no coincidence in opinion has yet been obtained as to the temperature range in which precipitation occurs. According to a comparatively recent study, C-curve is obtained when precipitations through reheating are plotted against the time required: Irvine and Pickering[8] obtained C-curve with the nose at about 700°C, and Smith[10] reported in detail C-curve obtained by careful experiments.

In Fig. 1 is shown C-curve obtained by the present authors. In the figure the carbide precipitation can be seen in a wide temperature range from 300 to 900°C, and the quickest rate of carbide precipitation is seen in the range from 650 to 700°C. At both sides of C-curve, the temperature range of precipitation becomes wider with the increase in the holding time, but the increase in the temperature range of precipitation becomes slight when the holding time is over 1 hour. Precipitation line for pearlitic constituent (or nodular pearlite, to be called P.C. hereafter) spreads out both upward and downward in the form of straight line at about 600°C as the peak, and the temperature range of precipitation increases with the increase of the holding time. Measurement of the lower side of C-curve was carried out up to 100 hours, and it is expected that in the case of measurement carried out up to a still longer time, the gradient of precipitation line of P.C. gradually becomes small until it becomes parallel to the time axis as is the case of carbide precipitation line. In the equilibrium state the upper side of precipitation line must coincide

with $A_{cm}$ line, but an inference may be made that it will take a long time to reach equilibrium in isothermal heating. $A_{cm}$ temperature was fixed at 925°C from the result of measurement of dilatation to be described later. The upper side of P.C. precipitation line becomes horizontal irrespective of the increase in the holding time. P.C. precipitation range could easily be determined by a simple magnetic method because of magnetism of $\alpha$ phase, and therefore, the equilibrium temperature for the upper edge of the precipitation line is inferred to be about 650°C.

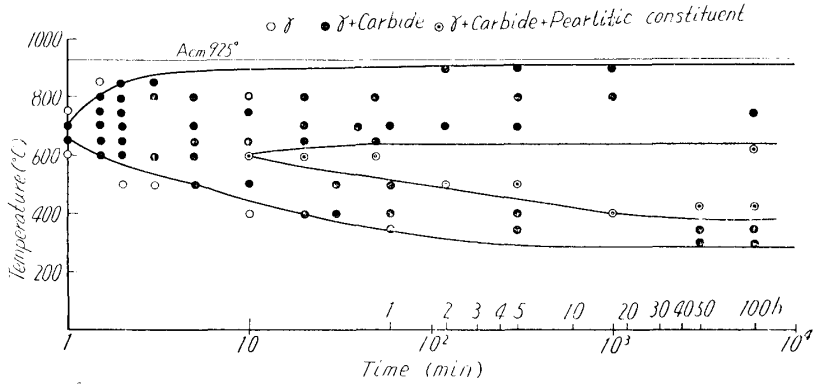



Fig. 1. Isothermal precipitation diagram for standard Hadfield steel after solution treatment.

It can be seen from Fig. 1 that precipitates obtained at low temperature range of 300 to 380°C and at high temperature range above 650°C were carbide, but that in the wide range of 380 to 650°C, carbide precipitated first of all, at the grain boundaries, and then P.C. when the precipitation continued for a long time. By comparing C-curve obtained by the present authors with the results by Smith[10] or by Irvine et al.[8], it will be seen that they coincide with each other in carbide precipitation line in most cases, but that the upper side of P.C. precipitation line lowers toward low temperature in the present case. This is because they concluded the carbide aggregation at about 700°C to be P.C. only from microscopic observations. But it is easily seen from the magnetic measurement mentioned above that $\alpha$ phase cannot be present at about 650°C.

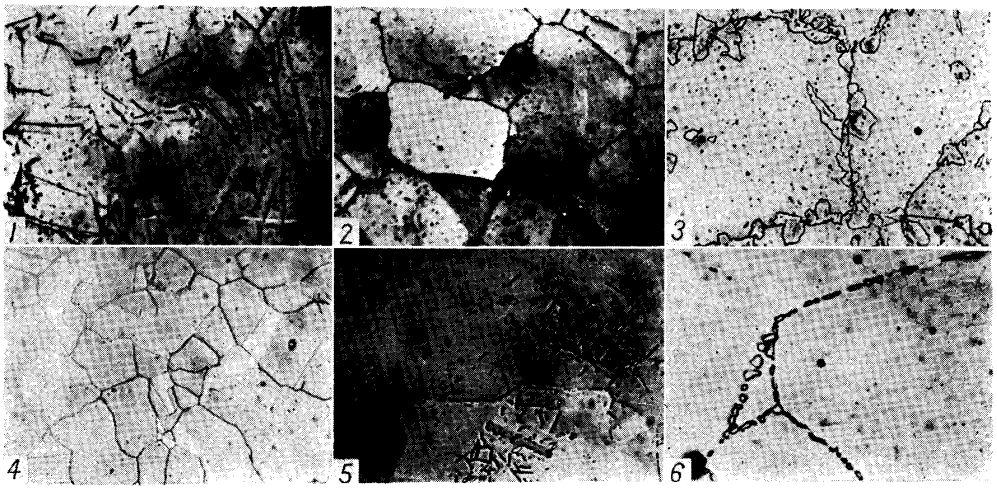
2. Form of precipitate

As mentioned above, carbide precipitates first in the all temperature ranges, and then P.C. Precipitates however, differed in form from each other according to the holding temperature. Carbide precipitated in the early stage as carbide film in austenite grain boundaries, showing the same form in the wide temperature ranges except in low temperature range. The formation of carbide film was very slow in the range below 400°C, and the growth could not be accelerated even by a long heating. With prolonged heating, needle-like carbide precipitation began at the grain boundaries along the cleavage plane gradually increasing the number, and appeared even in the grain. On the contrary, the formation of carbide film was quick in the range above 500°C and followed by the spherodization of carbide at the grain boundaries at temperatures above 650°C. At about 800°C, a change from the spherodization of

carbide to the separation in chain-like form occurred which was followed by growth and aggregation of spheroidal carbide. The tendency of spherodization of precipitated carbide was strong at high temperatures at which the diffusion of C is more remarkable, the spherodization in grain boundaries being 20 min at 700°C, 10 min at 750°C, 5 min at 800°C and 2 min at 850° C. However, at temperatures below 600°C, grain boundaries were covered by P.C. before carbide film grew into spherodization.

The precipitation may be observed in the needle-like form along the cleavage plane at the grain boundaries or in the grain. In general the needle-like precipitation began when the grain boundary precipitation was in far progress, and could clearly be observed immediately before and after P.C. precipitation line. However, in the low temperature range below 400°C, needle-like precipitates appeared in an early stage of precipitation as stated previously, and at high temperatures above about 800°C, needle-like precipitates was small and tended to spherodize.

Precipitation of P.C. was produced by nucleation at grain boundaries in P.C. precipitation line shown in Fig. 1, gradually growing into a nodular form. In an early stage of precipitation, P.C. spread from the nucleus formed at grain boundaries either grain or the other, and with the progress of growth some of them spread into other grain and their presence could be seen intermixed within grain boundaries. They appeared not only in grain boundaries but also in crystal grains, and are considered as being grown either from grain boundaries under surface of the specimens or from the nucleus formed around nonmetallic inclusions. Photo. 2 shows optical microstructures representative of the forms of precipitates described above.




1. 350°C×100hr, ×500 (1/2) 2. 650°C×5min, ×500 (1/2) 3. 600°C×50min, ×500 (1/2)
4. 700°C×5min, ×500 (1/2) 5. 800°C×16hr, ×500 (1/2) 6. 800°C×50min, ×1,500 (1/2)

Photo. 2. Representative optical microstructures for some carbide precipitated specimens.

Electron-microscopic form of needle-like carbide appearing in the low temperature range was like that shown in Photo. 3, showing a number of lines extending over the crystals at grain boundaries along the cleavage plane. Thus, it may be

considerd that carbide precipitates first in the form of thin platelet, and then gradually increases the thickness. For this reason, it is appropriate to call it platelet-like rather than needle-like. Photo. 4 shows the grain boundary carbide

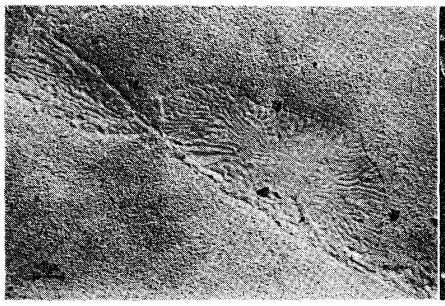
×10,000 (1/3)

Photo. 3. Platelet carbide, 350°C×100hr.

×10,000(1/3)

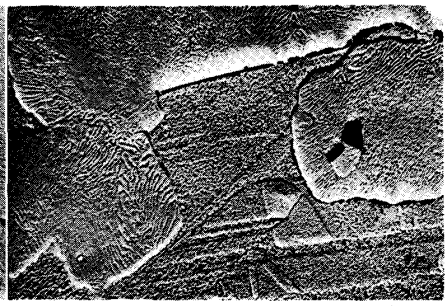
Photo. 4. Grain boundary carbide, 800°C×5min.

precipitated in the high temperature range. It has uniform surface, and no particular variations can be observed in it. Photo. 5 shows P.C. precipitated at 600°C, and Photo. 6 that precipitated at 500°C, both being observed under electronmicroscope. P.C. precipitated at 600°C has coarse lamellar, whereas that percipitated at 500°C has fine lamellar. As seen in the photograph the spaces of the lamellar are not uniform at some places, but measurements of spaces which were uniform showed them to be lamellar pearlite with such fine spaces as P.C. being 0.08 to 0.1$\mu$ at 600°C and 0.02 to 0.05$\mu$ at 500°C. It is impossible to detect the forms of lamellar even by means of electronmicroscope in an early stage of formation of the nuclear of P.C. Electronmicrostructure of P.C. has been reported by Kohn et al.[14] and formerly carbide in Hadfield steel was considered as only of $M_3C$ type, the composition being $(Fe, Mn)_3C+\alpha$ with saturated Mn, where $\alpha$ is regarded to be solute of Mn, as will be described later, the details of these carbide precipitates are being studied.



×10,000 (1/3)

Photo. 5. Pearlitic constituent precipitates at grain boundary, 600°C×50min.



×10,000 (1/3)

Photo. 6 Pearlitic constituent and $\varepsilon$, 500°C×100hr.

As seen in the precipitation line given in Fig. 1, the growth of the nucleus in P.C. precipitation is quickest at about 600°C, but after this stage, it can be said of the growth of P.C. that the lower the temperature is, the greater the growth rate

(14) A. Kohn, J. Plateau and G. Pompey, Compt. Rend., **242** (1956), 256.

is and that the rate reaches maximum at about 500°C.

It was confirmed by the measurement of the area ratio of P.C. precipitate in specimens held for the same time at various temperatures in P.C. precipitation range. According to Irvine et al.[8], the same area ratio line connecting the identical points of the area ratio of P.C. precipitate shifts downward to the right from P.C. precipitation line shown in Fig. 1.

P.C. kept on growing until it occupied the greater part of the area when it was held for a long time at the temperature at which the growth rate is greatest. Simultaneously $\gamma$ in the matrix became unstable gradually due to the decrease in the concentration of C and Mn through carbide precipitation, as a result of which two transfomations, namely, $(\gamma \rightarrow \alpha')$ and $(\gamma \rightarrow \varepsilon)$ appeared on water cooling, $\alpha'$ being martensite of *b.c.t.* structure, $\varepsilon$ being *h.c.p.* structure, and as the transformation $(\gamma \rightarrow \varepsilon)$ is martensitic, two martensite products come into existence. It is seen from these phenomena that the equilibirium phase at the temperature below the range of P.C. precipitation is ($\alpha$+carbide), but that it takes an extremely long time (inferred to be more than 5 years) to reach the equilibrium of ($\alpha$+carbide) even at about 500°C which is the temperature at which the growing rate of P.C. is greatest. Details will be reported in the later paper.

3. Precipitation through successive heating

Needless to say, it is very natural from isothermal precipitation diagram given in Fig. 1 that carbide precipities at such an early stage of heating that it is impossible to prevent carbide precipitation. In the case of Hadfield steel, a special consideration would be required at the time of heating because of their poor thermal conductivity. This necessitated an examination of precipitates appearing during successive heating. After solution treatment, the specimens were heated isothermally at various heating rates up to 1050°C by using the differential dilatometer, the variation points in the dilatation curve were observed and further microscopic exmaination and hardness measurement were made of the specimens water quenched.

Differential dilatation curves are shown in Fig. 2. As seen in the figure, the variations in expansion and contraction are most clear in the curve obtained at the most slow heating of 2°C/min. Moreover, an inflexion point is present at 300° C appearing as a contraction. This variation grew small with the increase in heating rate, but its presence was still observable, the temperature remaining fixed at 300°C. Such a obvious contraction observable in 2°C/min curve may suggest some sort of precipitation, but the fact was that the composition of the specimen water-cooled at 350°C was the same as that of the specimen solution-treated, and that the hardness remained unchanged. Contraction could not be observed in the specimen heated at 2°C/min and cooled at 400°C after passing the inflexion point at 300°C, and the inflexion point did not appear on further heating. No definite conclusion can be made on the cause of such a contraction, but an inference can be made that it is not related to precipitation but some variation in the matrix

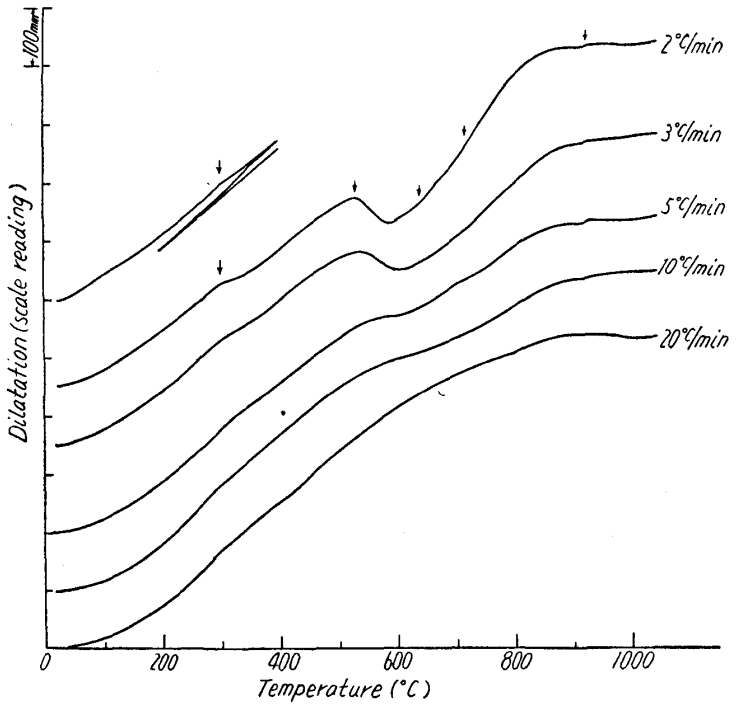



Fig. 2. Thermal dilatation curves in various heating velocities.

Another large contraction was observed beginning at 500°C and ending at about 600°C. With the increase in heating rate, the volume of contraction gradually decreased, shifting to the side of high temperature and disappearing altogether at 20°C/min. This contraction was caused by the precipitations of carbide at grain boundaries and of platelet carbide, and the former was small, but the latter was main cause of large valley at 600°C. This contraction was followed by the appearance of another very small contraction at about 640°C, which, considering from other experiments[15] by the present authors, seemed to be due to $\alpha$ phase precipitated as P.C. changing into $\gamma$ and dissolving in matrix. The evidence for this can be seen from the fact that a contraction is observable at about this temperature in the specimen in which a large amount of P.C. is precipitated on heating, and that in a magnetic test the specimen becomes non-magnetic at about this temperature. As stated previously, P.C. cannot be confirmed microscopically because it is very fine lamellar. If, however $\alpha$ precipitating as P.C. is considered to be exessively saturated by Mn, it can be explained the basis that $\alpha$-$\gamma$ transformation in Fe-Mn system has shifted pronouncedly to the side of low temperature by the increased amount of Mn.

The precipitation of carbide could be observed in a wide temperature range up to 925°C, but on reaching 720°C, it began to expand because of dissolving into $\gamma$, which comes to an end in the range above $A_{cm}$ line. The slower the rate of heating is, the larger the amount of precipitation is.

Fig. 3 shows the relation between time and variation point obtained from the dilatation curves described above. As seen in the figure, the variation at 300°C

(15) Y. Imai and T. Saitō, Japan Inst. Metals. Speech at 45th Conference.

is in the part of straight line independent of the rate of heating, and the curve showing the precipitation of carbide bends toward the side of high temperature with the increase of the rate of heating. When the rate of heating is raised above about 45°C/min, the curve does not cross the range of precipitation of carbide, and the carbide precipitation is not expected. The curve relating to precipitation of P.C. also bends toward the side of high temperature with increasing rate of heating, and it is conceivable that the precipitation of P.C. may not be observable above 15°C/min. $\alpha$–$\gamma$ transformation line is straight regardless of the rate of heating.

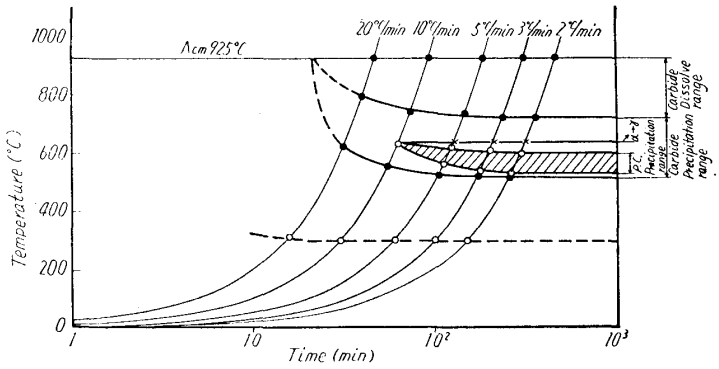


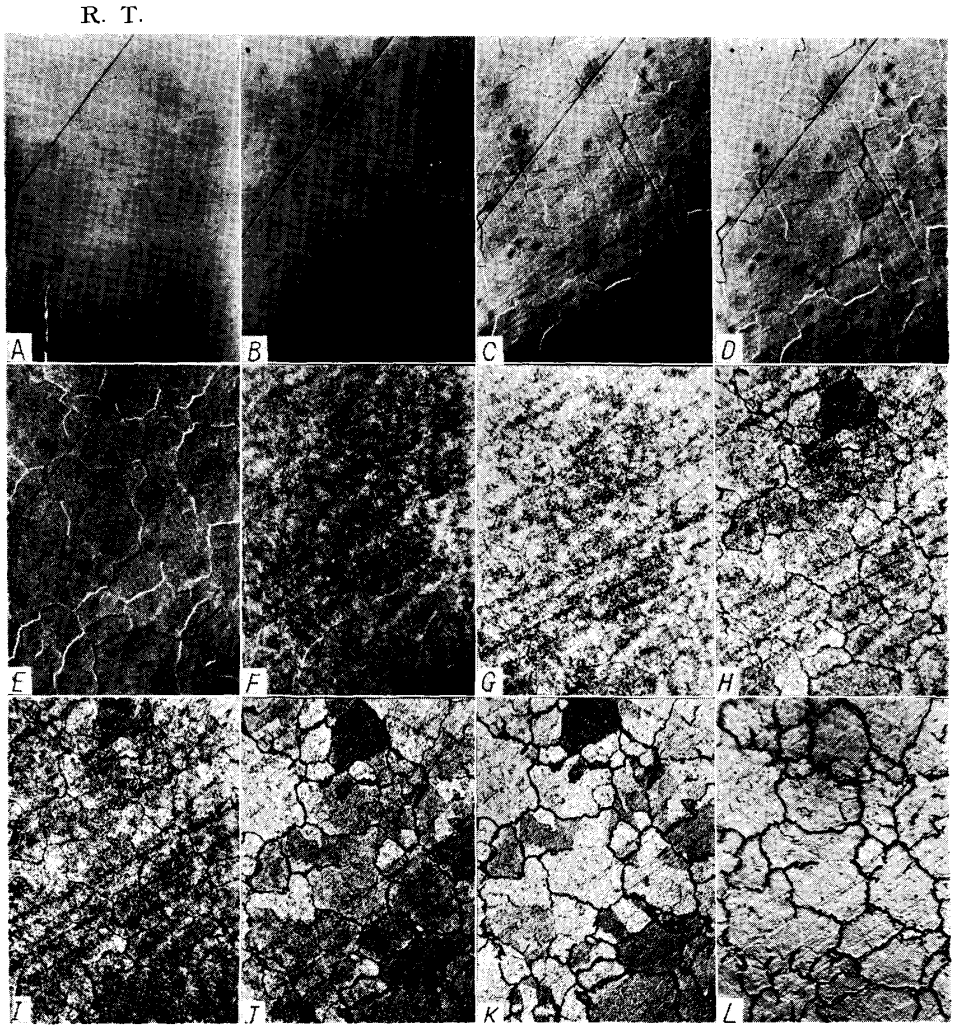

Fig. 3. Continuous heating precipitation diagram for solution treated steel.

4. Observation of precipitation under high temperature microscope

In order to make successive observations of the precipitation of carbide and P.C. during heating, solution-treated specimens heated at the rate of 3°C/min were examined under high temperature microscopy in each stage of precipitation, and it was found that the precipitation temperature in vacuum did not coincide with those mentioned above. Although the precipitation temperature coincided with those obtained by passing through argon, yet a fully satisfactory conclusion was not obtained.

Photo. 7 shows principal microstructures out of a series of structures observed. With the rise of heating temperature, the grain boundaries of $\gamma$-phase became visible, and at the same time inter-granular precipitation was observable in austenite grain as shown in (C). In this case it was due to anisotropy of thermal dilatation of crystal grains by heating that the grain boundary of $\gamma$ became visible microscopically. As shown in Photos. (D) and (E), a little inclination of light sourse will reveal that the surface of each grain is in relief. At this stage, carbide in grain boundaries has not appeared, but when the light source is turned upright, the marked precipitation of fine particles, which are no way related to austenite grain becomes observable (F). It is confirmed that this change begins at about 300°C, but no difinite assertion can be made as to whether the contraction in dilatation curve at 300°C is due to this change or not. This change is structure appears in patterns both dark and light and sometimes in those which are closely related to dendrite patterns. It has been reported[16][17] that Mn in the steel is segregated

(16) C. de Beaulieu and A. Kohn, Compt. Rend., **245** (1957), 1244.
(17) R. G. Ward, J. Iron & Steel Inst., **188** (1958), 337.




975°C
× 150 (1/2)

Photo. 7. Microstructure changes at high temperature for solution treated specimen.

in primary crystals. It has been also reported[18] that microscopic segregation of Mn is present in Hadfield steel. So, it is conceivable that this precipitation phenomenon of fine particles is related to microscopic segregation of Mn.

Following the precipitation both dark and light of fine particles, the precipitation of carbide appeared at grain boundaries (G), followed by the precipitation of P.C. (H). With the increase of heating temperature, the dissolving of P.C. began with the increase in intergranular precipitation (I). Intergranular precipitation was arranged in each grain, showing dark or light colour in the process of which the twin in austenite becomes easily discernible (J) (K). Furthermore, intergranular precipitates gradually dissolved into matrix and became uniform austenitic structure over the specimen surface (L).

After the dissolving of P.C., the grain boundary migration appeared, showing the change of straight grain boundaries of austenite into twisted boundaries after the dissolving of P.C. Photo. 8 shows an example of the grain boundary migration and

(18) W. Johnson and M. Andrews, Iron & Steel, **31** (1958), 437.

that of recrystallization at the surface scratch.

Grain boundary migration. ×500(1/2) Recrystallization at surface scratch. ×500 (1/2)

Photo. 8. Some microstructural changes by reheating.

In the above the processes of precipitation during heating has been explained. According to further experiments, a change was observed prior to the precipitation of carbide, which may be regarded as the precipitation of fine particles having no relation to crystal grain. This change is directly observable only in the specimen of highly heated state, but not in water-quenched specimen.

5. Effects of precipitation on mechanical properties

In Fig. 4 are shown mechanical properties of specimens heated for 1 hour at

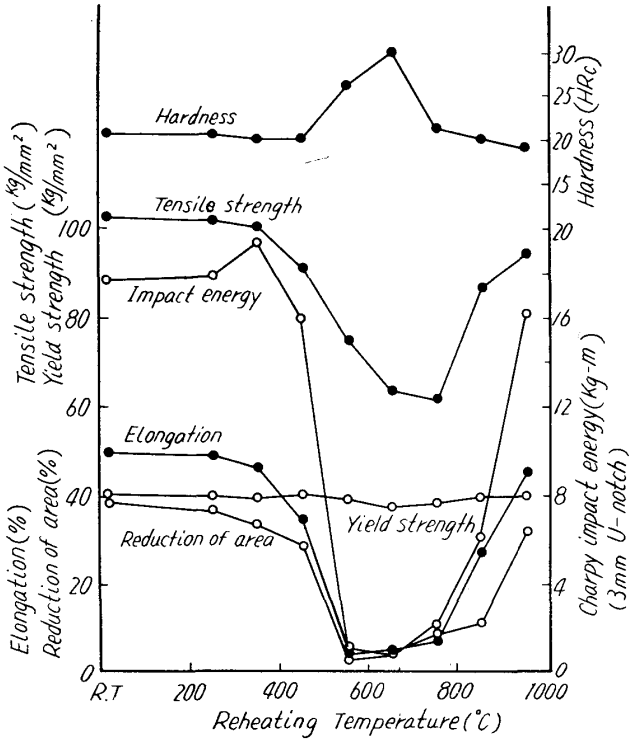



Fig. 4. Effect of reheating temperature on mechanical properties of solution-treated steel.

temperatures in the range of 250 to 950°C and water-quenched after solution treatment. Tensile strength begins to lower at about 350°C, at which the platelet carbide precipitates along the cleavage plane of crystal, reaching the lowest value at 750°C at which the carbide film shows the greatest growth in grain boundaries. After this point, it rapidly recovers but cannot be so high as in the state of solution

treatment even at 950°C. Yield strength remains almost unchanged in the whole range of temperature, but elongation and reduction of area remarkably lower in the precipitation range of carbide, similar to the case of tensile strength. Slightly differing from tensile strength, elongation and reduction of area reach the lowest value at about 550°C in the precipitation range of P.C. Impact value attains the lowest value in the P.C. precipitation range, forming an extremely large valley. On the contrary, hardness takes the highest value at 650°C, showing that the platelet carbide rather than P.C. has something to do with hardening.

## Summary

Precipitation of carbide by isothermal heating and successive heating of austenitic Hadfield Mn steel after solution treatment was examined. The results may be summarized as follows:

(1) The precipitation of carbide by isothermal heating was represented by C-curve with the peak at about 650° to 700°C, and P.C. by C-curve with the peak at about 600°C.

(2) Concerning the forms of precipitates, it may be said that in an early stage of precipitation, carbide film is formed at grain boundaries of austenite, but in low temperature range, the formation of carbide film is slow, producing plate-like precipitates along the cleavage plane from grain boundaries. In high temperature range, the formation of carbide film is followed by the spherodization of carbide film at grain boundaries and by the growth and aggregation of granular carbide.

(3) The nucleation of P.C. is most rapid at 600°C, and after this stage, the lower the temperature is, the more rapid the growth of P.C. is, reaching the greatest rate of growth at about 500°C.

(4) P.C. precipitated take the form of fine lamellar pearlite distinguishable by high magnification and the interlamellar spacing is smaller in those P.C. which are precipitated at lower temperatures.

(5) Precipitation during heating occurs at the side of high temperature and the quantity precipitated becomes less when the rate of heating is high. Heating at the rate of 15°C/min cannot produce P.C. and it is quite probable that the precipitation of carbide can be prevented if heating is done at the rate higher than 45°C/min.

(6) Mechanical properties begin to lower at about 350°C, at which the platelet carbide begins to precipitate. Tensile strength attains the lowest value at about 750°C, at which the growth of carbide film is most rapid. Impact value, elongation and reduction of area take the lowest values in the precipitation range of P.C. The platelet carbide is chiefly responsible for the increase of hardness by the precipitation of carbide.

In conclusion, the authors wish to extend their gratitude to Mr. Iwao Nakazawa for his hearty cooperation in the experiment.